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ANALYSIS OF POLYCYCLIC ORGANIC MATERIAL IN COAL, COAL ASH, FLY ASH, AND OTHER FUEL AND EMISSION SAMPLES

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16. ABSTRACT The report gives results of a high-resolution mass spectrometric investigation to determine the major polynuclear aromatic hydrocarbons (PNAs) in samples derived from various fuel conversion processes and related plant emissions. Studied were particulate materials and extracts of hydrocarbons in the particulate materials collected on filters placed in flue gas streams from coking, smelting, and similar industrial operations. The analysis considered 14 highly carcinogenic PNAs, with nine unique formulas. Additional quantitative data were obtained by low ionizing voltage techniques for major aromatic hydrocarbon classes, where possible. The gases evolved from the particulate samples were also identified.

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Analysis of Polycyclic Organic Material in Coal, Coal Ash, Fly Ash and Other Fuel and Emission Samples

Summary

The purpose of this high resolution mass spectrometric investigation was to determine the major polynuclear aromatic hydrocarbons (PNA) in samples derived from various fuel conversion processes and related plant emissions. Particulate materials and extracts of hydrocarbons in the particulate materials collected on filters placed in flue gas streams from coking, smelting, and similar industrial operations were studied. Fourteen highly carcinogenic PNA's, with nine unique formulas, were considered in the high resolution mass spectrometer analysis. Additional quantitative data were obtained by low ionizing voltage techniques for major aromatic hydrocarbon classes, where possible. The gases evolved from the particulate samples were also identified.

Possible carcinogens were detected in particulate material from four industrial sources. Nine formulas, indicating the possible presence of 14 highly carcinogenic PNA's, were observed in data for particulate matter collected at an aluminum plant. Eight of the formulas, corresponding to 12 carcinogens, were detected in the spectra of an extract of particulate material and a filter from the exhaust gas stream from ferroalloy operations. Data for 3 other extracts of particulate emissions from ferroalloy processing, CSL 7, 12, and 13, indicated the possibility of 5, 9, and 11 carcinogens, respectively. A pyridine extract of a filter from a chromium smelter and the tar from a coke oven vapor showed 1 and 4 possible carcinogens, respectively. No evidence of carcinogenic PNA's was detected in particulate material collected at the remaining 8 industrial sources. As_4O_6 was found in the particulate material associated with a copper smelter.

Introduction

Under an interagency agreement between the Environmental Protection Agency (EPA) and the U. S. Bureau of Mines (now Energy Research and Development Administration), a minimum of 10 samples, furnished by EPA, from various fuel emissions, and other processes was to be analyzed by high resolution mass spectrometry (HRMS) for polynuclear organic material. It was anticipated that some modification, adaptation, and improvement of existing technology would be required.

Polynuclear aromatic hydrocarbons (PNA) are associated with particulate emissions from many commercial processes. It is important to determine the nature of PNA's as many hydrocarbon mixtures derived from pyrolysis and other high-temperature operations contain hazardous compounds including carcinogenic components.

High-resolution mass spectrometry has the capability of determining the precise masses of the hydrocarbons from which the chemical formulas can be derived. While the elemental composition can be determined, the particular isomeric form cannot be identified from HRMS data alone. High resolution mass spectrometry can be used for the preliminary screening of complex mixtures

for the possible presence of several hundred hazardous and/or toxic compounds. Detailed analyses then need be carried out for only those components with formulas detected by HRMS. Major structural types including alkyl derivatives are determined quantitatively using low-ionizing voltage mass spectrometry.

In the current investigation, a screening technique has been devised and incorporated in the computer calculation of high-resolution data. Three hundred ten (310) compounds with low TLV values are included in addition to 14 carcinogens of specific interest. These 14 PNA's have 2-, 3-, and 4-star ratings in the NAS 1972 Handbook. Several of the compounds are isomers leaving 9 precise masses for detailed investigation by mass spectrometry.

Experimental Procedure

All data were obtained with a Dupont Model 21-110B high resolution mass spectrometer at 300° C, 10^{-6} torr. Mass spectra obtained at low resolution (1 part in 3,000) and recorded on strip charts were used for low ionizing voltage data which determines molecular ions for PNA's. The high resolution (1 part in 15,000) mass spectra were recorded on photographic plates and the data processed by computer using a program which calculates the precise masses of the ions present, determines their elemental composition, and screens the results for specific formulas corresponding to those of 310 toxic and hazardous compounds. High resolution mass spectral data can be summarized by plotting H vs. C for each formula occurring in the sample - a form of schematic representation. The number of hydrogen atoms in each hydrocarbon formula derived from the high-resolution mass spectral data is indicated by a point at the corresponding carbon number; a sequence of formulas at any one carbon number results in a continuous line. The position of the upper terminus of this line is indicative of the class of hydrocarbon compounds present in the sample. Figure 1 illustrates the limiting values for several compound classes. A schematic representation whose vertical lines approach line (a) indicates aliphatic hydrocarbons. Since the molecular ion of olefins and non-condensed naphthenes contains less hydrogen than the corresponding paraffins, the presence or absence of these compounds in a paraffinic matrix cannot be established by this method. Line (b), figure 1, is the limiting value for perhydroaromatic compounds and condensed naphthenes. The horizontal lines labeled (d) indicate the molecular ions of polynuclear aromatic hydrocarbons with varying degrees of condensation. Line (c) represents the terminus of lines for polynuclear aromatic hydrocarbons with a five carbon alkyl substituent. This line is an approximation since the number of hydrogens at a specified carbon number is determined by the degree of condensation of the polynuclear aromatic hydrocarbon. The carbon number distribution and hydrocarbon class of the sample components can be readily observed from schematic representations of high resolution mass spectral data.

Results and Discussion

The identification, source, and sample form of the samples investigated are shown in table 1.

EPA-1002 and EPA-72-001-159

The samples were first examined by direct vaporization using direct probe introduction. Components indicated in the gases obtained by direct vaporization are indicated in table 2. As very little volatile matter was detected in either sample at 300° C in the mass spectrometer, pyridine extraction of the samples was attempted. Extraction yields and also the percent of the extract vaporized in the mass spectrometer are given in table 2. The organic material obtained from both samples contained aliphatic, aromatic and oxygenated species. The upper carbon number limits found by mass spectrometry are shown in table 2. Both samples are complex mixtures of organic material. Sample 1002 appeared to contain a higher concentration of organic material which extended to higher carbon numbers than material from sample 72-001-159.

Both extracts were screened for formulas corresponding to possible hazardous and toxic components. The list prepared for the screening was derived from several of the current lists containing compounds with low TLV values. Preliminary screening of the two samples indicated molecular formulas for 12 possible hazardous components in sample 1002 and 6 in sample 72-001-159 as shown in tables 3 and 4. It should be emphasized that the screening technique is based upon a matching of molecular formulas and the particular isomeric form cannot be identified by high-resolution mass spectrometry. The value of this screening technique is that, within the sensitivity limits of the mass spectrometer, many highly toxic components can be eliminated from consideration. The analytical effort can then be concentrated on components for which molecular formulas corresponding to toxic components are indicated.

Coke oven vapor, run 2, stack 1

This coke oven vapor sample was studied by high-resolution mass spectrometry to determine if hazardous and toxic compounds are present. A summary of the high-resolution data is given in figure 2. The top series of lines that indicates the highest H/C values extends to approximately C_{20} and is indicative of highly saturated material. The lower series of lines results from components with a much lower H/C ratio, indicative of polynuclear aromatic material. This series of components extends to C_{22}. Trace components containing single oxygens were detected to C_{15}.

Screening of the high-resolution data gave formulas for the components given in table 5.

CSL-11

A sample of material extracted from a ferroalloy plant emission designated as No. CSL-11 was supplied as a dilute solution in methylene chloride; prior to analysis it was necessary to remove much of the solvent. The sample analyzed corresponded to 3.6% of the original solution.

The presence of possible carcinogenic PNA's was of particular interest. The HRMS data show 8 of the 9 precise masses of interest and a summary of the results including relative concentrations is given in table 6. The only formula not detected was $C_{21}H_{13}N$ at m/e 279, corresponding to the dibenzacridines. These HRMS data indicate that more specific follow-up techniques should be used for the other 12 compounds. The relative concentrations shown are based upon the best calibration data available. Anthracene/phenanthrene and pyrene/fluoranthene, m/e 178 and 202, respectively, were detected as major components in the sample. Table 7 is a summary of the data for the major structural types. The values include the alkyl derivatives. These data confirm that the highest concentrations are for the 3-, 4-, and 5-ring PNA's with peri-condensed structures such as pyrene and/or fluoranthene. Concentrations of the alkyl derivatives are much lower than for the basic ring structures; methyl derivatives are only a few percent of the basic ring structures. The ratio (derived from the mass spectral data) of unsubstituted to substituted rings is about 2.3:1.

CSL-7:72-003-110

Mass spectrometric analyses were obtained of a filter sample designated Ferroalloy CSL7:72-003-110. Three different sections of CSL-7:72-003-110 were examined to determine if the filter sample was homogeneous. The mass spectral data for the three sections from the filter sample indicate that the filter loading was not uniform, but that the emission particulates probably contain similar organic material throughout the exhaust stream. These conclusions are based on the data in table 8.

The 14 highly carcinogenic PNA's of interest were considered in the screening by high-resolution mass spectrometry. As shown in table 9, components with formulas corresponding to 8 of the 9 PNA's distinguishable by molecular formula were detected.

The sample was also examined by low ionizing voltage. The major structural types and percent of each are shown in table 10. Alkyl derivatives with 4 to 6 alkyl carbons were found for the major aromatic ring systems, with decreased concentrations as the number of alkyl carbons increased.

CSL-7, 12, 13 (Methylene chloride extracts)

Survey mass spectra of the three methylene chloride extracts of composited ferroalloy emission samples received from Battelle, Columbus confirmed their evidence that the PNA species varied in concentration among the samples (CSL-13>CSL-12>CSL-7). After removal of most of the solvent, both high-resolution and low ionizing voltage mass spectra were obtained.

The high-resolution mass spectrometric data from the 14 selected carcinogenic PNA's of particular interest are shown in table 11. Peak matching techniques at masses 267 and 279 confirmed the absence of nitrogen heterocycles.

Table 12 is a summary of the data for the major PNA's detected in the low ionizing voltage mass spectra, including alkyl derivatives. The distribution of the structural types is similar for all the extracts; the major difference among the extracts is the degree of substitution on the aromatic ring systems. The ratio of unsubstituted aromatic ring systems to substituted rings is 0.8:1 for CSL-7, while CSL-12 and CSL-13 have ratios of 3.64:1 and 2.87:1, respectively.

Series 11593

Mass spectrometric data were obtained for 14 particulate samples supplied by TRW under contract with the EPA. TRW prepared the samples collected from coking, smelting, and similar industrial sources, using 3 cyclones in series plus a backup filter to fractionate the particulates by size. Different particle sizes from the same source were examined.

Table 13 lists the percent of the particulate sample vaporized and the components observed in the mass spectra. Samples 14-4 and 14-5 showed intense mass peaks identified as As_4O_6, the dimer of As_2O_3. [1/] Some As_2O_3 may also be present although the intensity at the corresponding mass is much lower than that of As_4O_6. The presence of HCN, NO, NO_2, and COS in many of the samples may also be significant.

The distribution of the aromatic hydrocarbons observed in 16-4 is shown in table 14. Eighty-seven percent of the aromatic hydrocarbon content is concentrated in 4- to 6-ring aromatic systems. These data were obtained using low ionizing voltage techniques.

Pure compound studies of 4-, 5-, and 6-ring aromatic hydrocarbons, representative of those found in 16-3 and 16-4, have shown that their rate of vaporization in the mass spectrometer varies with both the number of aromatic rings in the molecule and type of condensation (peri or cata). Data shown in table 15 were obtained

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1/ Previously identified in Seattle ambient air. Schuetzle, D., A. L. Crittenden, and R. J. Charlson, J. Air Poll. Cont. Ass'n., vol. 23, August 1973, pp. 704-709.

from integrated peak height versus time curves for 16-3 and 16-4. Successive scans of the mass spectra were made over the period of time during which the sample continued to yield vaporization products. Ion intensities versus time were plotted and the area under the curves determined. These data also permitted corrections for the contribution of ^{13}C from the aromatic hydrocarbons to the molecular ions of the nitrogen containing compounds and determinations for small concentrations of these components not possible by the routine analytical method.

The computer data for the series 11593 were screened for the 9 precise masses indicating the possible presence of carcinogenic PNA's; table 16 shows the results of the screening. The mass spectra of the samples from the aluminum plant, 16-3 and 16-4, indicate the possibility of all of the carcinogenic PNA's as well as the typical aromatic hydrocarbons associated with electrode binder pitches listed in tables 14 and 15. The precise masses indicating possible carcinogens were not detected in any of the other samples.

CONCLUSIONS

Twenty-two samples of particulate material were analyzed by high resolution mass spectrometry for polycyclic organic material, including 14 highly carcinogenic polynuclear aromatic hydrocarbons.

A technique using HRMS to determine molecular formulas was successfully adapted to screening complex mixtures for carcinogens and other hazardous compounds. The technique is particularly amenable to the detection of PNA's because of their high sensitivity under mass spectrometric analysis. A major advantage of this technique is that the system can be completely automated to provide formulas for hundreds of compounds in mixtures.

Two limitations that are common to most types of mass spectrometer analysis are: (1) The compound must have at least minimal volatility (a few microns at 300° C, 10^{-6} torr) and (2) the compound must be stable under the above conditions of analysis. Mass spectral analysis of particulate material is limited by both volatility and stability. However, identification of gases evolved at 300° C, 10^{-6} torr provides some insight into the structure of the inorganic components of the particulate matter.

APPENDIX I

Tables

1. Identification, source, and form of samples investigated.

2. Mass spectrometric analyses of filter samples.

3. Screening of sample EPA-72-001-159 for possible hazardous compounds.

4. Screening of sample EPA-1002 for possible hazardous compounds.

5. Screening of coke oven vapor sample (Run 2, Stack 1) for possible hazardous compounds.

6. High-resolution mass spectrometric data for selected carcinogenic PNA's - Sample CSL-11.

7. Mass spectrometric analysis for PNA's in Sample CSL-11.

8. Mass spectral data for samples from CSL-7: 72-003-110.

9. High-resolution mass spectrometric data for selected carcinogenic PNA's - Sample CSL-7: 73-003-110.

10. Mass spectrometric analysis for PNA's in Sample CSL-7: 73-003-110.

11. High-resolution mass spectrometric data for selected carcinogenic PNA's in methylene chloride extracts of ferroalloy emission samples - CSL-7, 12, and 13.

12. Mass spectrometric analyses of PNA's in methylene chloride extracts of ferroalloy emission samples - CSL-7, 12, and 13.

13. Mass spectral information derived from Sample Series 11593.

14. Mass spectral analysis of EPA-TRW sample 11593-16-4.

15. Semi-quantitative mass spectral analysis of particulate matter collected in aluminum plant; integrated peak height versus time curves.

16. Results of mass spectral screening for carcinogenic PNA's - Series 11593: TRW Particulate Samples.

Figures

1. Limiting H/C values for several classes of hydrocarbon compounds.

2. High-resolution mass spectrometry data for coke oven vapor, run 2, stack 1.

Table 1. Identification, Source, and Form of Samples Investigated

No.	Identification	Source	Form
1	EPA-1002	Chromium smelter	Filter + pyridine extract
2	EPA-72-001-159	Ferroalloy plant	Filter + pyridine extract
3	Run 1, stack 2	Coke oven vapor	Tar
4	CSL-11 [a/]	Ferroalloy plant	CH_2Cl_2 extract
5	CSL-7:72-003-110	Ferroalloy plant	Filter
6	CSL-7	Ferroalloy plant	CH_2Cl_2 extract
7	CSL-12	Ferroalloy plant	CH_2Cl_2 extract
8	CSL-13	Ferroalloy plant	CH_2Cl_2 extract
9	11593-3-3 [b/]	Open hearth	Particulates
10	11593-3-4	Open hearth	Particulates
11	11593-4-4	Coke oven stack	Particulates
12	11593-7-4	Basic oxygen furnace	Particulates
13	11593-10-5	Iron sintering plant	Particulates
14	11593-10-6	Iron sintering plant	Particulates
15	11593-14-4	Copper smelter	Particulates
16	11593-14-5	Copper smelter	Particulates
17	11593-16-3	Aluminum plant	Particulates
18	11593-16-4	Aluminum plant	Particulates
19	11593-20-2	Ceramics plant	Particulates
20	11593-20-3	Ceramics plant	Particulates
21	11593-22-2	Municipal incinerator	Particulates
22	11593-22-3	Municipal incinerator	Particulates

a/ CSL denotes sample received from Battelle, Columbus Laboratories.

b/ 11593 designates samples received from TRW.

Table 2. Mass Spectrometric Analyses of Filter Samples

Sample	EPA-72-001-159	EPA-1002
% extracted in pyridine	< 1%	2%
% of extract vaporized in mass spectrometer	69%	100%
Compound type	Maximum carbon number detected	
Aliphatics	C_6	C_7
Aromatics	C_{14}	C_{18}
Oxygenates	C_8	C_{16}
	Gases detected	
Gases by direct vaporization from filter	CO	CO
	CO_2	CO_2
	HCl	SO_2
	SO_2	NO_2
	HN_3	NO
	H_2CO_3	H_2CO_3
	NO_2	HCl
	NO	HN_3
Possible toxic compounds [a/]	6	12

a/ Based upon formulas derived by high-resolution mass spectrometry; particular isomer not identified (see text).

Table 3. Screening of Sample EPA-72-001-159 for possible hazardous compounds

Precise mass	Formula	Possible hazardous or toxic compound[a/]
78.0468	C_6H_6	Benzene
98.0729	$C_6H_{10}O$	Mesityl oxide
106.0780	C_8H_{10}	Ethyl benzene
114.0678	$C_6H_{10}O_2$	Allylglycidyl ether
128.0624	$C_{10}H_8$	Naphthalene
178.0780	$C_{14}H_{10}$	Anthracene

a/ Particular isomer not identified (see text).

Table 4. Screening of Sample EPA-1002 for Possible Hazardous Compounds.

Precise mass	Formula	Possible hazardous or toxic compounds[a/]
92.0624	C_7H_8	Toluene
106.0789	C_8H_{10}	Ethylbenzene
108.0573	C_7H_8O	Cresol
118.0780	C_9H_{10}	Vinyltoluene
120.0936	C_9H_{12}	Cumene
128.0624	$C_{10}H_8$	Naphthalene
154.0782	$C_{12}H_{10}$	Diphenyl
170.0729	$C_{12}H_{10}O$	Phenyl ether
178.0780	$C_{14}H_{10}$	Anthracene/phenanthrene
202.0789	$C_{16}H_{10}$	Pyrene
228.0936	$C_{18}H_{12}$	Chrysene

a/ Particular isomer not identified (see text).

Table 5. Screening of Coke Oven Vapor Sample (Run 2, Stack 1) for Possible Hazardous Compounds.

Precise mass	Formula	Possible hazardous or toxic compounds[a/]
78.0463	C_6H_6	Benzene
92.0624	C_7H_8	Toluene
104.0624	C_8H_8	Styrene
106.0780	C_8H_{10}	Ethylbenzene
118.0780	C_9H_{10}	Vinyltoluene
120.0936	C_9H_{12}	Cumene
128.0624	$C_{10}H_8$	Naphthalene
138.0428	$C_6H_6N_2O_2$	Nitroaniline
148.1248	$C_{11}H_{16}$	P-Tert-butyl toluene
178.0780	$C_{14}H_{10}$	Anthracene/phenanthrene
202.0780	$C_{16}H_{10}$	Pyrene
228.0936	$C_{18}H_{12}$ [b/]	Chrysene
252.0936	$C_{20}H_{12}$ [b/]	Benzopyrene

a/ Particular isomer not identified (see text).

b/ Possible carcinogens.

Table 6. High Resolution Mass Spectrometric Data for Selected Carcinogenic PNA's - Sample CSL-11

m/e	Formula	Relative Concentration[a]	Possible Compounds
228	$C_{18}H_{12}$	12	Benzo(c)phenanthrene
252	$C_{20}H_{12}$	17	Benzo(b)fluoranthene Benzo(j)fluoranthene Benzo(a)pyrene
254	$C_{20}H_{14}$	1	Benz(j)aceanthrylene (cholanthrene)
256	$C_{20}H_{16}$	≤ 1	7,12-Dimethylbenz(a)anthracene
267	$C_{20}H_{13}N$	≤ 0.1	Dibenzo(c,g)carbazole
268	$C_{21}H_{16}$	< 0.1	3-Methylcholanthrene
278	$C_{22}H_{14}$	2	Dibenz(a,b)anthracene
279	$C_{21}H_{13}N$	-- [b]	Dibenz(a,j)acridine Dibenz(a,b)acridine
302	$C_{24}H_{14}$	1	Dibenzo(a,b)pyrene Dibenzo(a,i)pyrene Dibenzo(b,def)chrysene
		Additional PNA's - major components	
178	$C_{14}H_{10}$	14	Anthracene/phenanthrene
202	$C_{16}H_{10}$	17	Pyrene/fluoranthene

a/ Only relative concentrations determined.

b/ Not detected.

Table 7. Mass Spectrometric Analysis for PNA's in Sample CSL-11.

Structural type, including Alkyl derivatives	Weight, percent a/
Naphthalenes	0.06
Acenaphthylenes/fluorenes	.11
Acenaphthenes	.04
Anthracenes/phenanthrenes	.63
Phenyl naphthalenes	.21
Methylene phenanthrene	.02
4-rings, peri-condensed	.83
4-rings, cata-condensed	.54
5-rings, peri-condensed	.71
5-rings, cata-condensed	.10
6-rings, peri-condensed	.19
Binaphthyls	.13
Methylene chrysene	.02
6-rings, cata-condensed	.01
7-rings, peri-condensed	.01
Total	3.6

a/ Weight percent in solvent as submitted.

Table 8. Mass Spectral Data for Samples from CSL-:72-003-110

Sample	Percent vaporized a/	Maximum carbon number of aliphatic hydrocarbons	Maximum carbon number of total organic material	Maximum carbon number of oxygenated hydrocarbons
1	11.8	C_{15}	C_{29}	C_{27}
2	4.8	C_{14}	C_{27}	C_{26}
3	5.7	C_{12}	C_{26}	C_{25}

a/ Based on weight of filter plus sample.

Table 9. High Resolution Mass Spectrometric Data for Selected Carcinogenic PNA's - Sample CSL-7:72-003-110.

m/e	Formula	Relative concentration a/	Possible Compounds
228	$C_{18}H_{12}$	7	Benzo(c)phenanthrene
252	$C_{20}H_{12}$	9	Benzo(b)fluoranthene Benzo(j)fluoranthene Benzo(a)pyrene
254	$C_{20}H_{14}$	2	Benz(j)aceanthrylene (cholanthrene)
256	$C_{20}H_{16}$	2	7,12-Dimethylbenz(a)anthracene
267	$C_{20}H_{13}N$	2	Dibenzo(c,g)carbazole
268	$C_{21}H_{16}$	2	3-Methylcholanthrene
278	$C_{22}H_{14}$	3	Dibenz(a,b)anthracene
279	$C_{21}H_{13}N$	-- b/	Dibenz(a,j)acridine Dibenz(a,b)acridine
302	$C_{24}H_{14}$	3	Dibenzo(a,b)pyrene Dibenzo(a,i)pyrene Dibenzo(b,def)chrysene
		Additional PNA's	
178	$C_{14}H_{10}$	<1	Anthracene/phenanthrene
202	$C_{16}H_{10}$	7	Pyrene/fluoranthene

a/ Only relative concentrations available at this time.

b/ Not detected.

Table 10. Mass Spectrometric Analysis for PNA's in Sample CSL-7: 73-003-110.

Major structural types, including alkyl derivatives	% T. I. [a]
Naphthalenes	1.5
Acenaphthylenes/fluorenes	2.0
Acenaphthenes	1.8
Anthracenes/phenanthrenes	7.3
Phenylnaphthalenes	6.2
4-rings, peri-condensed	18.6
4-rings, cata-condensed	14.6
5-rings, peri-condensed	19.3
5-rings, cata-condensed	6.0
6-rings, per -condensed	14.6
Binaphthyls	5.8
6-rings, cata-condensed	0.7
7-rings, peri-condensed	1.6
Total	100.0

[a] Percent of total ionization assumes equal sensitivity for all components. Valid for comparison of similar samples.

Table 11. High Resolution Mass Spectrometric Data for Selected Carcinogenic PNA's in Methylene Chloride Extracts of Ferroalloy Emission Samples CSL-7, 12, and 13.

Mass	Formula	CSL-7	CSL-12	CSL-13 [a]	Possible Compounds
		Relative concentrations			
228	$C_{18}H_{12}$	9	17	14	Benzo(c)phenanthrene
252	$C_{20}H_{12}$	9	21	17	Benzo(b)fluoranthene Benzo(j)fluoranthene Benzo(a)pyrene
254	$C_{20}H_{14}$	[b]	1	1	Benz(j)aceanthrylene (cholanthrene)
256	$C_{20}H_{16}$	1	[b]	0.3	7,12-Dimethylbenz(a)anthracene
267	$C_{20}H_{13}N$	[b]	[b]	[b]	Dibenzo(c,g)carbazole
268	$C_{21}H_{16}$	[b]	[b]	2	3-Methylcholanthrene
278	$C_{22}H_{14}$	[b]	2	2	Dibenz(a,b) anthracene
279	$C_{21}H_{13}N$	[b]	[b]	[b]	Dibenz(a,j)acridine Dibenz(a,b)acridine
302	$C_{24}H_{14}$	[b]	1	1	Dibenzo(a,b)pyrene Dibenzo(a,i)pyrene Dibenzo(b,def)chrysene
		Additional PNA's			
178	$C_{14}H_{10}$	1.4	7	12	Anthracene/phenanthrene
202	$C_{16}H_{10}$	12.5	23	21	Pyrene/fluoranthene

[a] Only relative concentration available at this time.

[b] Not detected.

Table 12. Mass Spectrometric Analyses of PNA's in Methylene Chloride Extracts of Ferroalloy Emission Samples CSL-7, 12, and 13.

Major structural types, including alkyl derivatives	CSL-7	CLS-12	CSL-13
	Percent of total ionization		
Naphthalenes	-	-	-
Acenaphthylenes/fluorenes	-	-	1.6
Acenaphthenes	-	-	1.2
Anthracenes/phenanthrenes	10.6	12.0	16.5
Phenylnaphthalenes	7.2	4.3	4.7
4-rings, peri-condensed	26.5	28.3	26.8
4-rings, cata-condensed	18.0	21.0	17.7
5-rings, peri-condensed	18.6	23.3	19.4
5-rings, cata-condensed	4.9	2.6	2.7
6-rings, peri-condensed	7.5	5.6	5.7
Binaphthyls	5.0	2.7	3.4
6-rings, cata-condensed	-	0.2	0.2
7-rings, peri-condensed	1.6	< 0.1	0.3
Ratio $\frac{\text{Unsubstituted aromatic rings}}{\text{Substituted aromatic rings}}$	0.8	3.64	2.87

Table 13. Mass Spectral Information Derived from Sample Series 11593.

Sample	Particle size, μ	Origin	Percent Vaporized	Summary of high resolution and low Ionizing voltage mass spectral data: Gases evolved at 300° C, 10^{-6} torr	Hydrocarbon Formulas Identified [a]
3-3	3	Open hearth furnace	2.1	HCN, CH_3CN, HCl, CO_2, NO_2, EtOH, CH_3COOH, SO_2, COS, CO	Pyridine, C_5-C_7, aliphatic radials, trace oxygenates
3-4	1	Open hearth furnace	0.12	HCN, CH_3CN, HCl, NO, NO_2, H_2S, CO_2, EtOH, CO, COS, SO_2, CS_2	Pyridine, MePyridine; aliphatic hydrocarbon radicals through C_7 Six unidentified mass peaks < mass 102; trace oxygenates
4-4	1	Coke oven	5.3	HCN, CH_3CN, CO, NO, H_2S, CO_2, NO_2, SO_2, COS, C_6H_6, CS_2	Pyridine, Mepyridine, C_7-C_8 naphthenes, aliphatic radicals through C_6; unidentified mass peaks < mass 109.
7-4	1	Basic oxygen furnace	3.2	HCN, CH_3CN, CO, NO, HCl, CO_2, NO_2, EtOH, SO_2, COS	Pyrrole poss., trace oxygenates, trace hydrocarbons through C_9
10-5	3	Iron sintering plant	7.3	HCN, CH_3CN, CO, NO, H_2S, HCl, CO_2, NO_2, EtOH, SO_2, COS	C_6H_6, $C_{10}H_8$, $C_{11}C_{10}$, $C_{14}H_{10}$
10-6	1	Iron sintering plant	37.8 [b]	HCN, CH_3CN, CO, NO, HCl, CO_2, NO_2, EtOH, SO_2, COS, H_2S	C_6H_6, $C_{10}H_8$, $C_{11}H_{10}$, $C_{14}H_{10}$, C_6H_6O
14-4	1	Copper smelter	n.a. [c]	SO_2, CS_2, CO, CO_2	As_4O_6
14-5	3	Copper smelter	n.a. [c]	HCN, CO, HCl, NO_2, SO_2, CS_2, COS	AS_4O_6
16-3	1	Aluminum plant	1.3	CHN, CO, NO, HCl, CO_2, NO_2, SO_2, COS, H_2S	Aromatic hydrocarbons; nitro- and sulfur heterocyclics (see table 1)
16-4	3	Aluminum plant	5.2	CHN, CO, NO, HCl, CO_2, NO_2, SO_2, COS	Similar to 16-3 in composition; slightly lower carbon number distribution for all classes of compounds
20-2	1	Ceramics plant	2.4	HCN, CO, NO, MeOH, HCl, SO_2, NO_2, H_2S, COS	Trace organics through C_{10}
20-3	3	Ceramics plant	2.1	HCN, CO, NO, HCl, CH_3CN, CO_2, EtOH, NO_2, SO_2, COS, H_2S	Pyridine, trace organics through C_{10}
22-2	1	Municipal incinerator	4.0	HCN, CO, NO, HCl, CH_3CN, CO_2, NO_2, SO_2, CS_2	Pyrrole, phenol, aromatics through C_{10} aliphatic radicals through C_8
22-3	3	Municipal Incinerator	0.5	HCN, CO, NO, H_2S, HCl, CH_3CN, CO_2, NO_2, COS, SO_2, CS_2	Trace hydrocarbon

[a] All isomeric structures are possible
[b] Measurement doubtful
[c] n. a. - not available.

Table 14. Mass Spectral Analysis of EPA-TRW Sample 11593-16-4

Possible structural types	Percent total ionization [a]
Benzenes	1.1
Naphthalenes	0.4
Acenaphthylenes; fluorenes	0.8
Acenaphthenes; biphenyls	1.0
Anthracenes; phenanthrenes	3.8
Phenylnaphthalenes	2.5
4-rings, peri-condensed	10.2
4-rings, cata-condensed	10.4
5-rings, peri-condensed	39.9
5-rings, cata-condensed	12.5
6-rings, peri-condensed	14.0
7-rings, peri-condensed	0.4
Carbazoles	0.9
Dibenzocarbazoles	0.9
Dibenzacridines	1.1

[a] Distribution of PNA's in portion of sample vaporized in the mass spectrometer.

Table 15. Semi-Quantitative Mass Spectral Analysis of Particulate Matter Collected in Aluminum Plant; Integrated Peak Height Versus Time Curves

	11593	
Sample number	16-3	16-4
Percent vaporized	4.5	3.7
Particle size, μ	1	3
Weight collected, mg.	983.3	1,613.6

Examples of structural types	Percent of total ionization	
3-ring aromatics	2.3	0.8
Phenylnaphthalenes	2.3	5.4
4-ring, peri-condensed	6.5	7.5
4-ring, cata-condensed	7.0	7.0
5-ring, peri-condensed	20.4	12.4
Phenylanthracenes	3.5	12.0
5-ring, cata-condensed	12.6	13.3
6-ring, peri-condensed (mass 276)	17.1	3.7
6-ring, peri-condensed (mass 302)	3.5	2.5
7-ring, peri-condensed (Coronene)	1.1	0.9
Dinaphthothiophene	1.5	1.6
Azapyrene + Benzocarbazole	12.2	12.5
Benzacridine	1.3	5.7
Carbazole	1.0	1.9
Acridine	1.2	3.2
Dibenzocarbazole	1.4	0.4
Dibenzacridine	0.8	3.1
Azabenzo[ghi]perylene	0.03	2.1
Azaperylene	4.3	4.0

Table 16. Results of Mass Spectral Screening for Carcinogenic PNA's - Series 11593: TRW Particulate Samples

Sample [a]		16-3	16-4
Nominal Mass	Formula		
228	$C_{18}H_{12}$	X[b]	X
252	$C_{20}H_{12}$	X	X
254	$C_{20}H_{14}$	X	X
256	$C_{20}H_{16}$	X	X
267	$C_{20}H_{13}N$	X	X
268	$C_{21}H_{16}$	X	X
278	$C_{22}H_{14}$	X	X
279	$C_{21}H_{13}N$	X	X
302	$C_{24}H_{14}$	X	X

a/ Entire sample series screened for carcinogenic PNA's. None detected in samples of particulates from sources other than the aluminum plant.

b/ Molecular formulas verified by precise mass measurement.

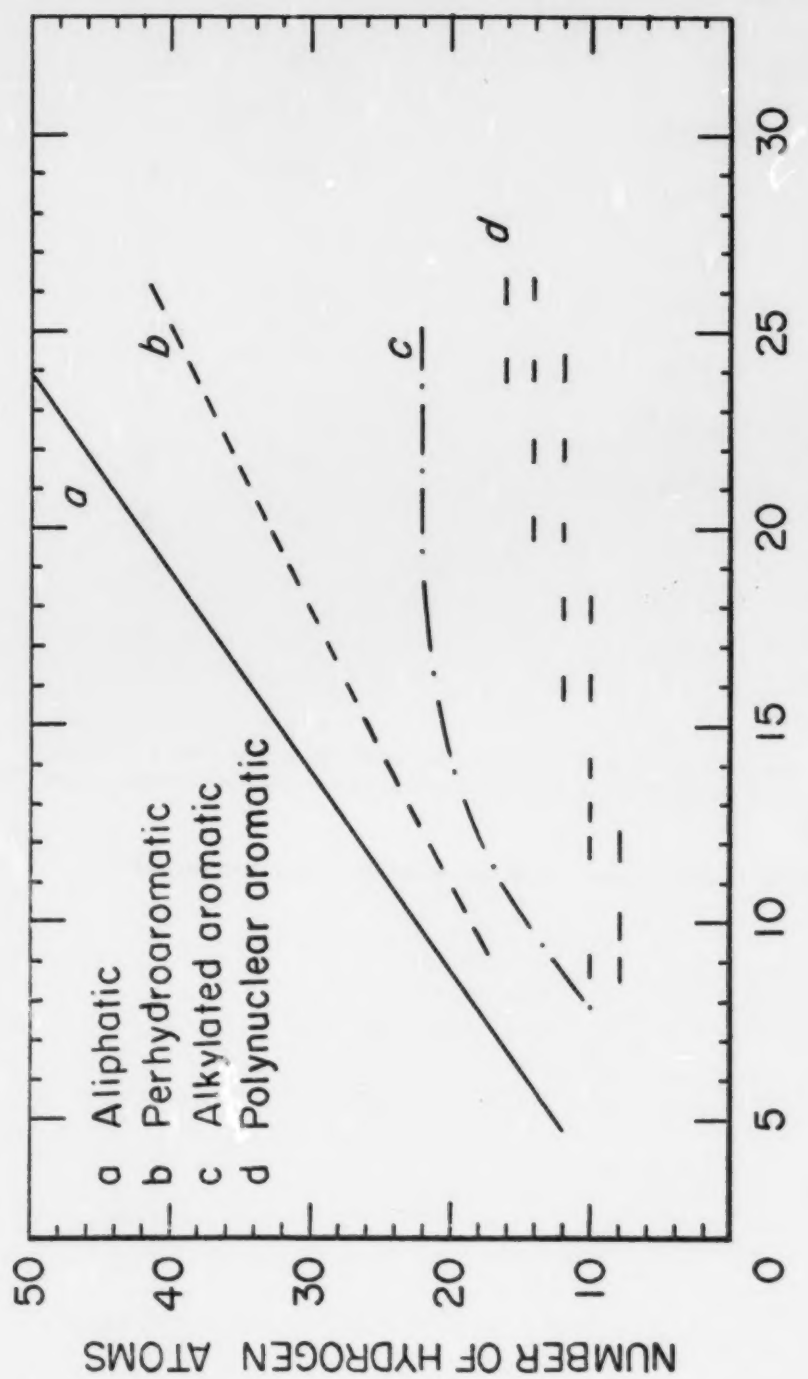

Figure 1. Limiting H/C values for several classes of hydrocarbon compounds.

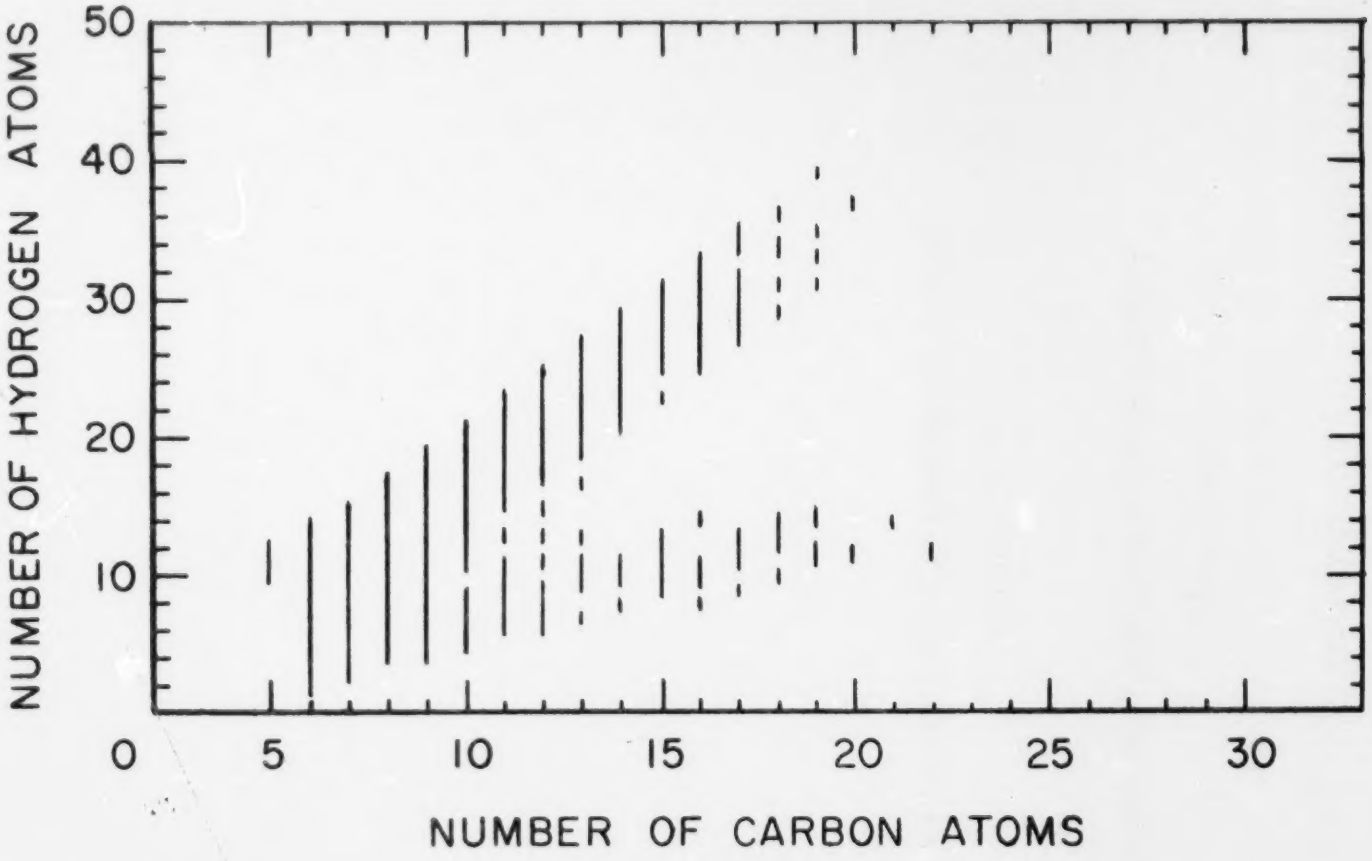

Figure 2. High-resolution mass spectrometry data for coke oven vapor, run 2, stack 1.

Visitors

None.

Personal Mention

None.

APPENDIX II

Manuscripts in preparation and/or published.

None.

APPENDIX III

Nonexpendable items consisting of $100 or more.

None.